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ABSTRACT

This study investigated secondary air pollutants formed from reactions between constituents of terpene-containing household products and ozone. Gas-phase emissions from three different products were introduced along with ozone into a 198-L Teflon-lined reaction chamber. Gas-phase concentrations of reactive terpenes, terpenoids and oxidation products were measured. When the formulation contained more than one reactive VOC, their relative consumption by ozone was proportional to the initial reactant concentrations and to the rate constants of the respective terpene-ozone reactions. Formaldehyde was a predominant oxidation byproduct for the three studied products. Acetaldehyde and acetone were also detected when two of the products were exposed to ozone. A scanning mobility particle sizer measured particle nucleation events followed by a significant degree of ultrafine particle growth immediately upon mixing of reactants. Elevated concentrations of OH radicals generated by terpene ozonolysis were also measured.

INDEX TERMS

Terpenes, ozone, formaldehyde, reactive chemistry, secondary organic aerosols.

INTRODUCTION

The use of cleaning products and air fresheners indoors can cause inhalation exposure of cleaning personnel and building occupants to toxic air contaminants (TACs). In addition to direct inhalation of toxic constituents of the product, many products contain terpene hydrocarbons and terpenoids that can react rapidly with ozone, yielding secondary pollutants. Ozone is commonly present indoors owing to infiltration of outdoor air and ventilation. Indoor sources of ozone also exist, including some photocopy machines and “air purifiers.” The products of ozone reactions with terpenes and terpenoids include volatile carbonyls, some of which are TACs (e.g., formaldehyde and acetaldehyde). Ozone-terpene reactions also produce the hydroxyl radical, which potentially can lead to the formation of additional TACs.

Little is known about the indoor concentrations of TACs as secondary pollutants from cleaning products and air fresheners (Nazaroff and Weschler, 2004). Exposure concentrations to such secondary pollutants depends on the complex interplay of many factors and processes, including product composition, usage, emission dynamics, transport and mixing, building ventilation, sorptive interactions with building surface, and reactive chemistry. The goal of

this study is to provide experimental information on the latter, specifically on the rate and extent of the formation of secondary pollutants from terpene-containing household products in the presence of moderate and high ozone levels.

EXPERIMENTAL METHODS

The reaction of ozone with cleaning product/air freshener components was studied in a 198-L stainless-steel flow reaction chamber, internally lined with FEP-Teflon film to minimize sorption effects. The chamber was operated under positive pressure and was provided with two inlet ports on opposite corners. A constant flow of air and the product gas-phase components were introduced into one of them, and an air stream containing ozone was admitted at the other inlet. Chamber temperature and RH were measured and continuously recorded. The experimental setup was housed in a 20-m³ environmental room. Chamber temperatures were consistently in the range 23.0 ± 0.5 °C. The main airflow to the chamber, of compressed “zero quality” air, was split between a dry and a humidified stream and adjusted using mass flow controllers to obtain a RH between 40 and 60 %. Well-mixed conditions within the chamber were demonstrated with SF₆, which was introduced at either inlet and continuously monitored at the outlet using an infrared analyzer.

Ozone was generated by means of UV irradiation of an airstream flowing at 100 cc/min. Immediately before and after each run, the ozone inlet concentration was measured directly employing a calibrated ozone monitor, to determine the amount of O₃ introduced in the chamber and to verify its stability during the experiment. Otherwise, the ozone monitor continuously sampled from the chamber outlet and the data were logged at 1-min intervals.

Three common US retail products containing ozone-reactive chemicals were employed in this study: a general-purpose pine-oil-based cleaner, an orange oil-based degreaser containing d-limonene as the sole active ingredient, and a plug-in scented-oil air freshener. The gas-phase components of the first two products were delivered to the reaction chamber from an 80-L Tedlar bag prepared by adding a measured amounts of the cleaning product and air, followed by heating in an incubator at 50 °C for 2 h. A peristaltic pump delivered a constant flow (in the range 20-100 mL/min) into the main airflow. For the plug-in air freshener, an 80-L stainless steel drum replaced the Tedlar bag. Inside the drum, the product was continuously electrically powered, as it would be in ordinary use, and a stream of air circulating at 100 mL/min introduced the volatile components into the main air stream. 1,3,5-Trimethylbenzene and perchloroethylene were generated with diffusion tubes placed in a thermostat at 40 °C and supplied at constant rates to the reaction chamber. These chemicals were used to estimate the concentration of OH radical in the system (Weschler and Shields 1997).

Sampling of VOCs was performed using two Tenax®-TA tubes connected in parallel immediately after the outlet port. Two adjacent sampling ports were used to collect samples on DNPH-coated silica cartridges preceded by an ozone scrubber to determine volatile carbonyls and on NaOH-coated silica cartridges to determine volatile carboxylic acids (ozone-scrubbing was determined not to be necessary for the Tenax sampling). Sorbent tubes were analyzed by thermal desorption-gas chromatography-mass spectrometry (TD/GC/MS). Quantification of VOCs was performed through calibration curves using authentic standards, with bromofluorobenzene serving as an internal standard for quantification. Calibration curves were linear for the studied VOCs in the ranges 5-150 ng. DNPH-coated cartridges were extracted with 2 mL acetonitrile. DNPH-carbonyl derivatives present in the extracts were analyzed at 360 nm by HPLC provided with a UV diode-array detector. NaOH-coated

silica cartridges were extracted with deionized water, and the extracts were analyzed by ion chromatography using an anionic exchange column.

Particles in the diameter range 8-400 nm were sampled from the chamber air and analyzed in real-time with a Scanning Mobility Particle Sizer (SMPS).

We investigated the effect of two parameters on each of the three studied products: reaction time using air change (ach) rates of 1 h^{-1} and 3 h^{-1} , and the ozone level using 130 and 60 ppb inlet concentrations. The initial VOC concentrations in the reaction chamber were determined at the beginning of each experiment with air from the cleaning product or air freshener source supplied, but in the absence of ozone. Subsequently, ozone was introduced at a constant flow rate. A second steady-state condition was attained, and a second measurement of concentrations was made. Consumption of the reactant and the yield of products were calculated from the difference between concentrations measured in the presence and absence of ozone.

RESULTS AND DISCUSSION

In Table 1 we present data obtained from experiments with the pine oil-based cleaner in the presence of moderate and high ozone levels and at low and high reaction rates (i.e., $\text{ach} = 3\text{ h}^{-1}$ and 1 h^{-1} respectively). The values shown on the concentration (C) column correspond, in the case of ozone, to its chamber concentration in the absence of reactive VOCs, and for VOCs to the initial steady-state concentration before addition of ozone. The concentrations indicated for oxidation products are measured at steady state in the presence of the cleaning product components and ozone. Similarly, the second column indicates the fraction of ozone and of VOCs that reacted in each case (as the ratio between its final and initial concentration), and the % yield of oxidation products. The latter is determined as the ratio between the steady-state concentration of the product and the ozone concentration in the absence of reactants.

For the six main VOC components presented in Table 1, three reacted substantially and unambiguously in the high ozone experiments. Eucalyptol and p-cymene were relatively inert, as is consistent with expectations based on their bimolecular rate constants with ozone. The results for α -terpineol for the high ozone, high air exchange condition suggest a reactivity towards ozone that is similar to that of d-limonene. However, the results are not consistent among the two high ozone experiments. Considering the three remaining VOCs, all monoterpenes, in the high ozone experiments about 90 % of the α -terpinene was consumed, while roughly 30 to 40 % of the terpinolene and 15 to 20 % of the d-limonene were consumed. For these three species, the relative reactivity was reasonably proportional to the product of their concentration and their reported reaction rates with ozone: 2×10^{-14} , 2×10^{-15} and $2 \times 10^{-16}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$, respectively (Shu and Atkinson 1994). Ozone was substantially titrated by the excess reactive VOCs in all our experimental conditions. Consistent with expectations, the table reveals that across all three experiments the observed extent of reaction depended more on the ozone level than on the reaction time.

Formaldehyde and acetaldehyde are listed as hazardous air pollutants by the USEPA and as toxic air contaminants by the California EPA. California's chronic reference exposure levels for those two TACs are 2 ppb and 5 ppb, respectively (OEHHA, 2000). Although the conditions employed in this study are artificial, the reactant concentrations are not unrealistic. Under these conditions, those reference levels were exceeded in all cases. Formaldehyde levels in this work were also higher than 17 ppb, the recommended 8-hour occupational exposure level in the US (NIOSH).

Table 1. Reaction of ozone with pine oil-based cleaner components.

	High ozone; 3 ach		High ozone; 1 ach		Low ozone; 3 ach	
	C (ppb)	% reacted (or % yield)	C (ppb)	% reacted (or % yield)	C (ppb)	% reacted (or % yield)
ozone ^a	131 ± 4	90 ± 7	130 ± 13	94 ± 15	65.1 ± 2.1	97 ± 11
VOC components ^b						
α-terpinene	24.9 ± 1.4	92.1 ± 3.2	25.1 ± 1.9	88.5 ± 4.2	23.5 ± 2.2	72.1 ± 6.6
d-limonene	219 ± 2	17.4 ± 0.7	229 ± 6	14.5 ± 2.3	206 ± 5	1.20 ± 3.8
p-cymene	41.3 ± 0.5	1.2 ± 1.3	41.6 ± 1.6	1.6 ± 3.1	36.5 ± 1.7	-4.4 ± 5.2
eucalyptol	57.6 ± 0.4	3.3 ± 0.5	60.3 ± 1.7	2.6 ± 2.5	46.3 ± 9.3	-19 ± 13
terpinolene	266 ± 12	42.5 ± 3.0	266 ± 14	33.2 ± 4.0	236 ± 32	8 ± 12
α-terpineol	149 ± 4	13.7 ± 2.2	104 ± 3	-9.3 ± 2.2	154 ± 25	-2 ± 11
Volatile oxidation products ^c						
formaldehyde	34.5 ± 1.0	28.4 ± 0.9	35.4 ± 0.5	27.2 ± 0.4	13.3 ± 0.5	20.4 ± 0.8
acetaldehyde	7.3 ± 3.6	6.0 ± 2.9	12.2 ± 1.5	9.3 ± 1.1	5.5 ± 0.9	8.4 ± 1.4
acetone	80.5 ± 4.5	66.2 ± 3.7	82.6 ± 2.8	63.4 ± 2.1	28.9 ± 1.1	44.5 ± 1.7
formic acid	26.5 ± 4.4	21.8 ± 3.6	11.8 ± 5.4	9.1 ± 4.2	10 ± 15	15 ± 23
acetic acid	38.1 ± 7.4	31.4 ± 6.1	22 ± 12	17.1 ± 9.3	3 ± 22	5 ± 33

Concentrations (C) are reported for these conditions:

^a Ozone level in reaction chamber without cleaning products;

^b VOC components in reaction chamber without ozone; and

^c Volatile oxidation products in reaction chamber with ozone and VOC components combined.

A similar outcome was observed for the reaction of ozone with the volatile components of the other two studied products. In the case of the degreaser, d-limonene was the only active ingredient, yielding also high levels of formaldehyde, but not appreciable amounts of acetaldehyde, as expected. The formulation of the plug-in air freshener was the most complex among the studied products, with more than 30 volatile components. However, only four of those components exhibited reactivity toward ozone, including linalool and d-limonene, the two most reactive ingredients. Linalool is a slightly more reactive molecule ($k = 4 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) than d-limonene and had about a two-fold higher concentration. As a consequence, linalool was consumed to the largest extent. Other (minor) reactive species in the air freshener were dihydromyrcenol and linalyl acetate.

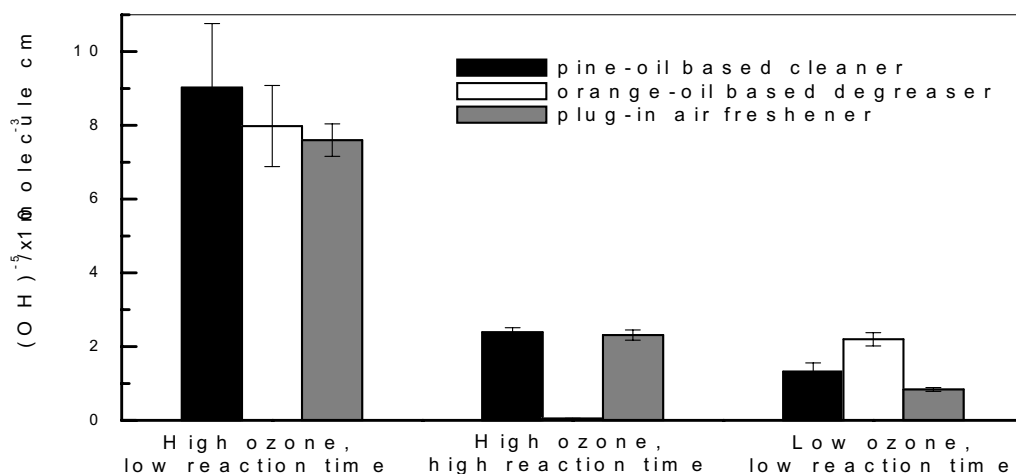


Figure 1. Evaluation of OH radical concentrations.

We determined the concentration of OH radicals in the system through its reaction with 1,3,5-trimethylbenzene (indicator) in the presence of perchloroethylene (added as inert reference). Figure 1 shows the (OH) concentrations measured at each condition for the three products. These results are consistent with previous measurements by Weschler and Shields (1997) employing d-limonene and ozone mixtures. Our results suggest that the OH yield is not linearly proportional to the ozone concentration: between 3- and 7-fold increases were observed when the ozone level rose from ~ 65 to ~ 130 ppb, with the same reaction time (i.e., $\text{ach} = 3 \text{ h}^{-1}$). A longer reaction time (i.e., $\text{ach} = 1 \text{ h}^{-1}$) substantially decreased the OH concentration. This decrease is apparently related to the lower residual level of ozone.

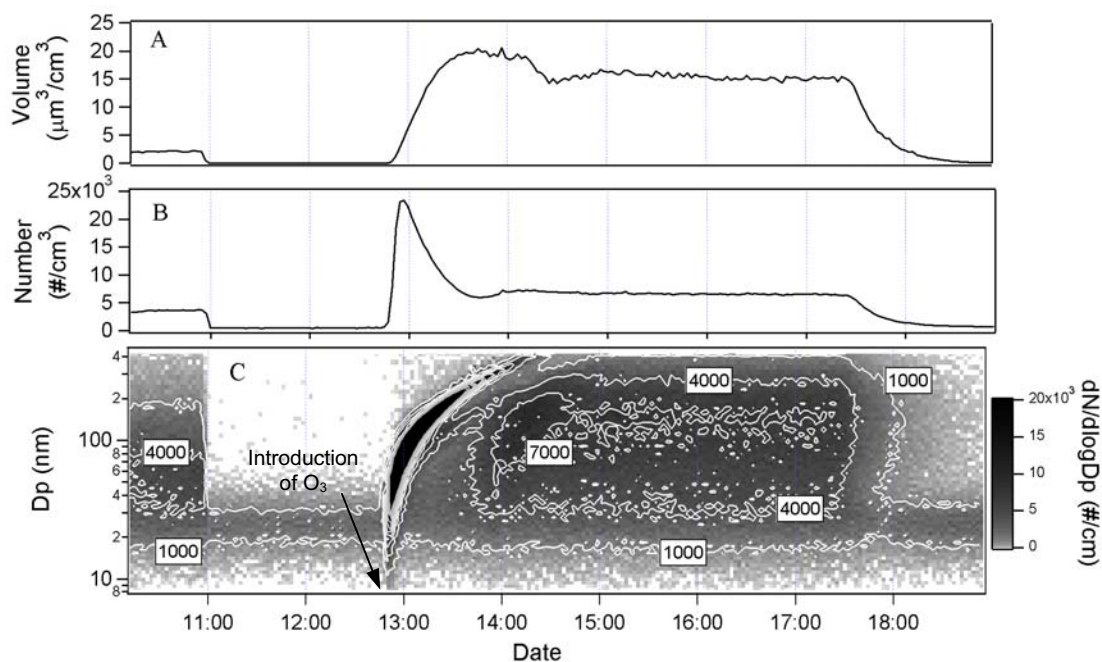


Figure 2. SMPS measurement for particles from the air freshener VOCs with moderate ozone. Total number and volume concentration were calculated by integration from the size distribution, and therefore do not account for particles that have grown out of the measurement range of the instrument.

Figure 2 shows the temporal evolution of aerosol particle volume (A), number (B) and size distribution (C) for an experiment where the plug-in air freshener volatile components were exposed to moderate ozone levels (60 ppb before addition of VOCs). Similar curves were obtained for the other products and for other experimental conditions. The most distinctive feature in all cases was the large burst of ultrafine particle nucleation and growth that occurred immediately upon ozone addition (indicated with an arrow in frame C). The number of particles measured at the peak of the burst was found to be proportional to the ozone level in all cases. Remarkably, the observed production of ultrafine aerosol particles in these studies is similar in its main features to nucleation events observed in the atmosphere (Kulmala et al 2004; Kavouras et al 1998).

CONCLUSIONS

These experiments showed that building occupants are potentially exposed to secondary pollutants due to the interaction of atmospheric ozone with terpenes and terpenoids present in household product formulations. Quantitative measurements of the levels of toxic air contaminants that are produced by these reactions at several conditions were obtained. In addition, we observed the formation of OH radicals and a large burst of ultrafine particulate matter as a consequence of ozone-terpene reactions. Being the limiting reagent under realistic experimental conditions, ozone is essentially titrated by the excess reactive VOCs. Therefore, for the conditions of this study, the production of secondary pollutants depends primarily on the ozone level, and is less influenced by other parameters such as the air change rate.

ACKNOWLEDGEMENTS

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